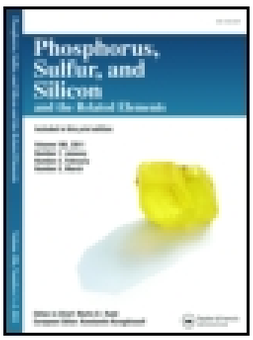

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Reactions of quinones with some amino alcohols, thiols and a UV-Vis study

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ABSTRACT

In the present study, the reactions of 2,3-dichloro-1,4-naphthoquinone (DCNQ) with amino-1,2-propanediol and some thiols were investigated. Novel N-, N,S-, and S,O- substituted derivatives were obtained and the structures of all compounds were characterized by spectroscopic methods (FT-IR, ^{1}H NMR, ^{13}C NMR, Mass spectroscopy) and microanalysis. The absorption behaviors of novel compounds were also investigated with UV-Vis spectroscopy in different solvents, such as ethanol, tetrahydrofuran and chloroform.

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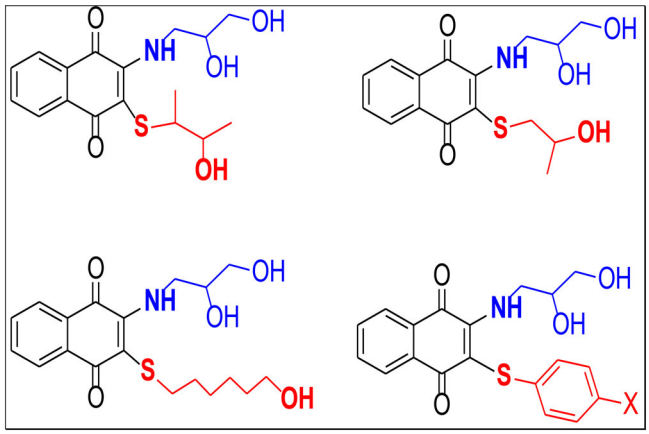
Thiols; amino alcohols; 23-dichloro-14-naphthoquinone; UV-Vis spectroscopy

GRAPHICAL ABSTRACT



Introduction

Amino alcohols (alkanolamines) are important compounds in chemistry that contain both amine and alcohol functional groups. Simple alkanolamines are used as solvents, synthetic intermediates, and high-boiling bases.[1] Different amino alcohol derivatives have been used for the synthesis of many important compounds in medicinal chemistry.[2,3] The synthesis of some immunosuppressive active amino alcohol derivatives by using Ullman and Suzuki reactions has been reported in the literature.[4] The best known and most important drug derivative of an amino alcohol moiety, which is used in the treatment of tuberculosis (TB), is (2,20 ethylenediiminodi-1-butanol) Ethambutol (EMB).[5] The remarkable activity increase with using enantiomerically pure beta-amino alcohols has been reported in organic synthesis.[6–9] The other important intermediate which we have used in our studies is the 2,3-dichloro-1,4-naphthoquinone moiety. It has been reported that quinones show a remarkably broad spectrum of pharmacological activities such as antimalarial, antifungal, antibacterial and antitumor properties.[10–15] The moderate activity of *N*-substituted quinones against lung cancer A549 cells has recently been reported.[16] Besides that, many procedures based on activation of thiol by a base in the reaction with quinones have been studied.[17–19] In this study, we tried to combine these three important agents *viz*, naphthoquinone unit, amino alcohols and thiols. The novel compounds were fully characterized using spectroscopic techniques.

Results and discussion

The reaction of 2,3-dichloro-1,4-naphthoquinone (1) with 5-mercapto-1-methyltetrazole (2) in Na_2CO_3 mixture of ethanol gave *S,O*- substituted compound (3). The methyl protons attached to the nitrogen ($-NCH_3$) protons of compound (3) were observed at 4.10 ppm in the ^{1}H NMR spectrum. The mass spectra of (3) in the positive ion mode for ESI confirmed the proposed structures; the molecular

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ion was observed at m/z 317 (100%). Methyl piperazynyl substituted compound (5)[20] and *N*- substituted compound (9)[21] have been obtained from the 2,3-dichloro-1,4-naphthoquinone (1) and related nucleophiles. The IR spectra of compound (9) showed a broad band at 3454 cm^{-1} indicating the interference of characteristic hydroxyl and amine groups. The molecular ion peaks of compounds (5) and (9) were identified at m/z 291 and 280 (%100), respectively (Scheme 1).

N,S-substituted naphthoquinone derivatives (7a-f) were synthesized from the starting compound (5) and various thiols (6a-f). The ester carbon of compounds (7a) and (7b) gave characteristic peaks at 1732 and 1736 cm^{-1} in the IR spectra. The characteristic –OH band was seen at 3385 cm^{-1} for compound (7c) in the IR. The molecular ion peaks of compounds (7d) and (7e) were observed at m/z 383 and 445(100%) in the positive ion mode of ESI, respectively. The ^{13}C NMR spectra of (7f) showed two carbon signals for the carbonyl groups at 179.18 ppm (Cl-C-CO-C-O) and 180.55 ppm (O-C-CO-C-O). 2,3-dichloro-1,4-naphthoquinone (1) was reacted with 3-amino-1,2-propane diol (8) and known compound (9) was obtained in our previous study.[21] The amino substituted compound (9) was reacted with some thioalcohols such as 6-mercapto-1-hexanol (10), 3-mercapto-2-butanol (14) and 1-mercapto-2-propanol (16) and final N,S- substituted products (11), (15), and (17) were isolated. The interference of characteristic hydroxyl and amine bands were seen at 3373 cm^{-1} in the IR spectrum of compound (11). The mass spectra of (15) in the positive ion mode for ESI confirmed the proposed structure; the protonated molecular ion was observed at m/z 352 (%100) (Scheme 2).

The ^{13}C NMR spectra of (17) showed two carbon signals for the carbonyl groups at 180.51 and 179.04 ppm. The molecular ion peaks of compounds (19a) and (19b) were observed at m/z 374 and 433 in the positive ion mode of ESI, respectively. The IR spectrum of compound (20) showed a broad band at 3326 cm^{-1} which indicates the presence of –NH and –OH groups. The compound (9) was also treated with some thiols and novel compounds (21) and (26) were achieved. The characteristic ester bands of these compounds were seen at 1731 and 1729 cm^{-1} in the IR spectra, respectively. Unexpected *S,O*- substituted compound (25) was obtained when compound (9) was reacted with tert-dodecyl mercaptan (24) instead of the formation of a *N,S*- substituted compound (Scheme 3).

The molecular ion peak with sodium adduct of compound (25) was observed at m/z 425 in the mass spectrum. The same behavior was observed in the reaction of (9) and a diamine (22). The difunctional nucleophile (22) expelled the amino alcohol substituent from the structure (9) and generated the cyclic product (23). The molecular ion peak of compound (23) was seen at m/z 325 in the positive mode of ESI.

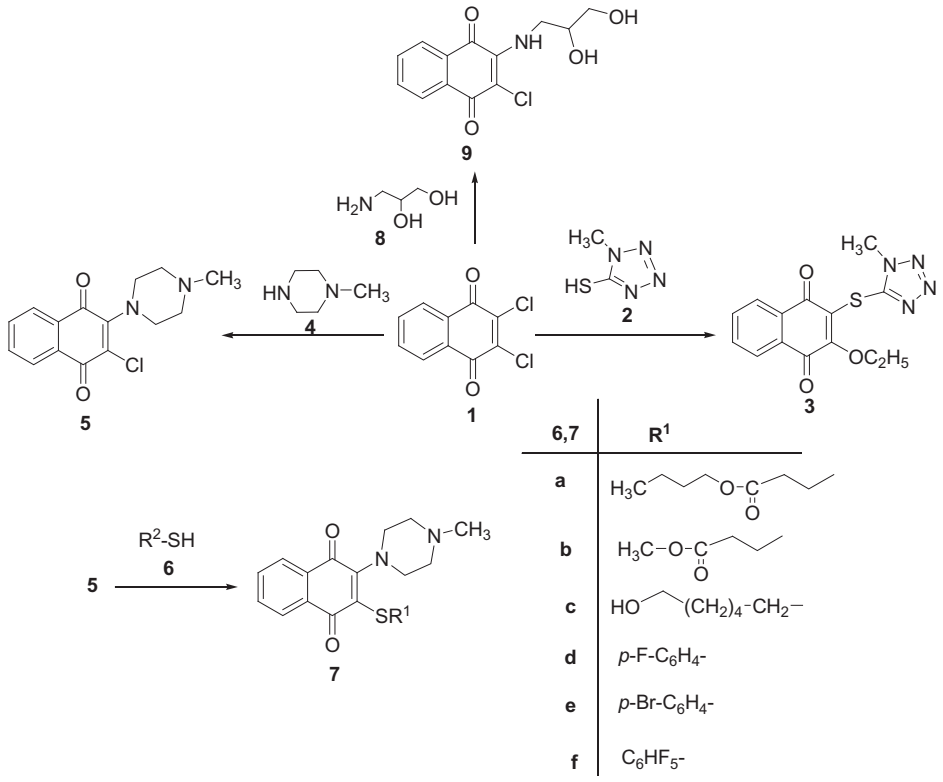
The absorption characteristics of some available quinone derivatives were studied by using UV-Vis spectrometer in different solvents. The evaluation of the spectra shows that the absorption bands of the quinone derivatives can be divided into three groups: The maximum energy bands at around 278-260 nm, broad intense bands at around 382-338 nm region, and the low broad visible bands at around 436-547 nm.[22] The long wavelength absorption bands at around 383 and 344 nm can be assigned to a π-π^* transitions of quinonoid structure.[23,24] Changes for absorbances to a longer wavelength have been measured when polar solvent is used. Especially in ethanol solutions the compounds exhibited a weak absorption bands at around 438-483 nm. The slight shoulders or extreme weak absorptions at the longer wavelength are an indication of the n-π^* transitions.[23] The electronic absorption spectra of (9) showed the expected naphthoquinone bands in the UV region around 254 nm and at 338 nm (π- π^* transitions electronic transitions). In addition, a third lower energy transition appeared as a broad band in the visible region at 470 nm. This absorption is typical of amino-substituted quinone[25] and is assigned to CT transitions and weak n–p* transitions. As can be seen in supplementary material Table S1, compound (20) showed strong bathochromic shifts relative to the *N*-substituted quinone compound (9) in ethanol solution. The result can be explained the electron-donating effect of sulfur and the other oxygen atom on the thio-substituent. UV-Vis data for some compounds are shown in supplementary material Table S1.

Experimental

Melting points were measured using a Buchi B-540 melting point apparatus and are uncorrected. Elemental analysis were performed on a Thermo Finnigan Flash EA 1112 elemental analyzer. The IR studies were carried on a Thermo Scientific Nicolet 600 FTIR spectrometer in the range of 400 to 4000 cm^{-1}. UV-Vis studies were performed on Perkin Elmer Lambda 35 UV/Vis Spectrometer. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in $CDCl_3$ on a Varian Unity INOVA spectrometer. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS spectrometer using the ESI technique. Products were isolated by column chromatography on Sigma silica gel 60, pore size s70-230 µm. Thin-layer chromatography (TLC) was performed on Merck silica gel plates 60 F254 and detection was carried out with ultraviolet light (254 nm). All chemicals were reagent grade and used without further purification.

General procedures

General procedure 1. 2,3-dichloro-1,4-naphthoquinone **(1)** 1.0 g (2.033 mmol)**, (5)** or **(9)** and corresponding nucleophile were stirred in ethanol (50 mL) with Na_2CO_3 (1.52 g) for 5-6 h at room temperature. The color of the solution quickly changed and the reaction was monitored by TLC. Chloroform (30 mL) was added to the reaction mixture. The organic layer was washed with water (4 × 30 mL), and dried over Na_2SO_4. After the solvent was evaporated the residue was purified by column chromatography on silica gel.



Scheme 1. Synthesis of new amino- and thio-substituted quinones.

General procedure 2. 2,3-dichloro-1,4-naphthoquinone **(1)** 1.0 g (4.40 mmol) and corresponding nucleophile were stirred in chloroform (30 mL) with triethyl amine (3 mL) for 5-6 h at room temperature. The color of the solution quickly changed and the reaction was monitored by TLC. Chloroform (30 mL) was added to the reaction mixture. The organic layer was washed with water (4 × 30 mL), and dried over Na_2SO_4. After the solvent was evaporated the residue was purified by column chromatography on silica gel. The supplemental materials contain samples of ^1H and ^{13}C NMR spectra, FT-IR and mass spectra for the products 3 – 26 (supplemental materials Figures S1 – S75).

2-(1-methyl-1H-tetrazol-5-ylthio)-3-ethoxynaphthalene-1,4-dione (3) was synthesized from 2,3-Dichloro-1,4-Naphthoquinone (**1**) (1.0 g, 2.033 mmol) and 5-Mercapto-1-methyltetrazole **(2)** (1.02 g, 4.066 mmol) by use of the general procedure 1.

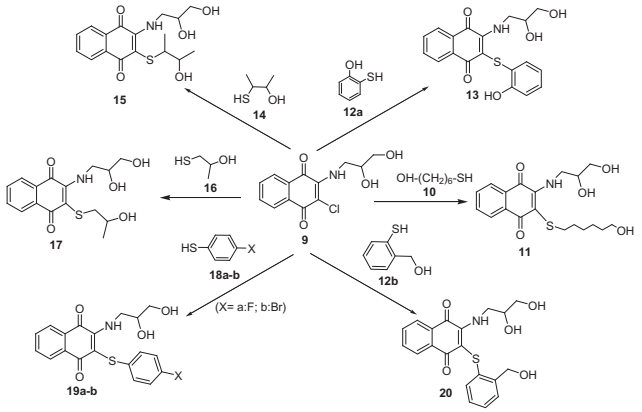
Red Solid. Yield: 1.33 g (65%). Mp.: 149-150 °C. *Rf*: 0.47 [$CHCl_3$]. IR (KBr): 3019 (N-N), 2926 (C-H), 1672 (C = O), 1551 (C = C). ^1H NMR (499.74 MHz, $CDCl_3$): 1.22-1.25 (m,-CH_3), 4.55 (q, J = 6.83 Hz, -OCH_2) 4.10 (s, 3H, -NCH_3), 7.63-7.97(m, 4H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 14.76 (-CH_3), 33.38 (-NCH_3), 70.34 (-OCH_2), 133.46, 133.42, 132.98, 132.97, 130.56, 130.11, 126.01, 125.93, 125.89, 125.84, 125.83, 123.25 (C_{arom}, CH_{arom}), 179.53, 178.21 (C = O). MS [+ESI]: m/z = 317 $[M+H]^+$, $C_{14}H_{12}N_4O_3S$ (Mw = 316.34 g/mol) = Calculated: C, 53.16%; H, 3.82%; N, 17.71%; S, 10.14% Found: C, 53.24%; H, 3.55%; N, 17.21%; S, 9.86%.

2-chloro-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione (5)[20] was synthesized from 2,3-Dichloro-1,4-Naphthoquinone (**1**) (1.0 g, 2.033 mmol) and 1-Methylpierazine **(4)** (0.22 mL, 2.066 mmol) by use of the general procedure 2.

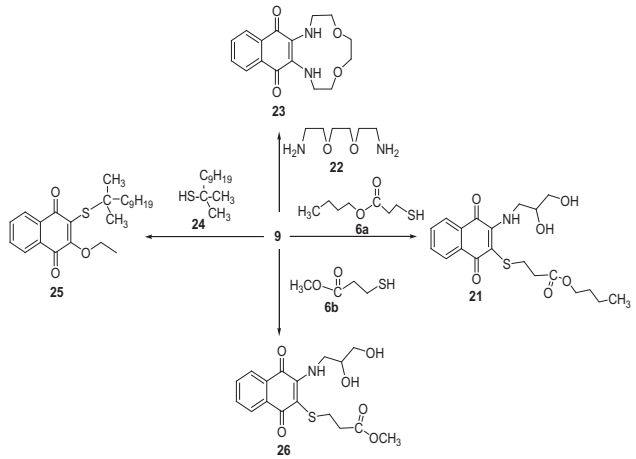
Red Solid. Yield: 0.62 g (86%). Mp.105-106 °C (Lit[20] for **5**.HCl m.p. 220-225 °C). *Rf*: 0.48 [EtAc]. IR(KBr): 3014 (C-$H_{arom.}$), 2938, 2848 (C-H), 1675 (C = O), 1557 (C = C). ^1H-NMR (499.74 MHz, $CDCl_3$): δ = 2.31 (s,3H, -NCH_3), 2.58 (t, J = 8.78, 4 H, -NCH_2), 3.56 (t, J = 9.76, 4 H, -NCH_2), 7.87 (dd, J = 6.34, 6.84, 2 H, H_{arom}), 7.98 (dd, J = 6.34, 8.30, 2 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 46.17 (-NCH_3), δ = 55.76, 51.23 (-NCH_2), 134.25, 133.28, 131.74, 131.59, 127.04, 126.80, 126.70, 123.38 (C_{arom}, CH_{arom}), 181.94, 178.10 (C = O). MS [+ESI]: *m/z* = 291 $[M+H]^+$, $C_{15}H_{15}ClN_2O_2$ (Mw= 290.74 g/mol) Calculated: C, 61.97%; H, 5.20%; N, 9.64% Found: C, 61.84%, H, 5.33%; N, 9.43% .

Butyl-3-(1,4-dihydro-2-(4-methylpiperazin-1-yl)-1,4-dioxonaphthalen-3-ylthio)propanoate (7a) was synthesized from 2-chloro-3-(4-methylpiperazin-1-yl)naphthalene-1, 4-dione (**5**) (0.1 g, 2.033 mmol) and Butyl-3-mercapto-propionate **(6a)** (0.056 mL, 2.066 mmol) by use of the general procedure 1.

Purple Oil. Yield: 0.115 g (73%). *Rf*: 0.54 [EtAc]. IR (KBr): ν = 3065 (C-H), 2958, 2933, 2873, 2794 (C-H), 1732 (C = O_{ester}), 1668(C = O), 1537(C = C). ^1H-NMR (499.74 MHz, $CDCl_3$): 0.83 (m,3H, -CH_3), 1.28-1.55 (m, 4 H, -CH_2), 2.37 (s, 3 H, -NCH_3), 2.51 (t, J = 7.32, 4 H, -NCH_2), 3.10 (t, J = 7.32, 4 H, -NCH_2), 3.96 (t, J = 6.83, 2 H, -OCH_2), 3.53 (t, J = 7.32, 2 H, -SCH_2),7.54 (dd, J = 6.34, 6.84, 2 H, H_{arom}), 7.97 (dd, J = 6.34, 8.30, 2 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 19.3(-CH_3), 34.38, 33.51, (-CH_2), 45.93 (-NCH_3), 35.74 (S-CH_2), 55.53, 51.87 (-NCH_2), 69.38 (-OCH_2), 133.93, 133.13, 132.26, 126.82, 126.54, 125.18



Scheme 2. Synthesis of amino-alcohol derivatives with thiols.



Scheme 3. Novel *N,S*- and *S,O*- substituted quinones.

(C_{arom}, CH_{arom}), 182.01, 181.88 (**C**=O). MS [+ESI]: m/z = 417 $[M+H]^+$, $C_{22}H_{28}N_2O_4S$ (Mw = 416.53 g/mol) = Calculated: C, 63.44%; H, 6.78%; N, 6.73%; S, 7.70% Found: C, 63.36%; H, 6.45%; N, 6.50%; S, 7.13%.

Methyl 3-(1,4-dihydro-2-(4-methylpiperazin-1-yl)-1,4-dioxonaphthalen-3-ylthio)propanoate (7b) was synthesized from 2-chloro-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione **(5)** (0.1 g, 2.033 mmol) and Methyl-3-mercapto-propionate **(6 b)** (0.041 mL, 4.066 mmol) by use of the general procedure 1.

Purple Oil. Yield: 0.109 g (77%). R*f*: 0.52 [$CHCl_3$]. IR (KBr): 3069(-CH_{arom}), 2927, 2849, 2797 (C-H), 1736 (C = O_{ester}), 1668 (C = O), 1537 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 2.37 (s,3H, -NCH_3), 3.54 (t, J = 7.31, 2 H, -SCH_2), 2.53 (t, J = 7.32, 4 H, -NCH_2), 3.07 (t, J = 7.32, 4 H, -NCH_2), 3.60 (s, 3 H, -CH_3), 7.55 (dd, J = 6.34, 6.84, 2 H, H_{arom}), 7.96 (dd, J = 6.34, 8.30, 2 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 55.48 (-OCH_3), 29.67 (-CH_2), 34.98 (S-CH_2), 45.87 (N-CH_3), 51.99, 51.97 (-NCH_2), 154.61, 135.01, 133.95, 133.14, 132.98, 132.54, 132.24, 127.07, (C_{arom}, CH_{arom}), 181.97, 172.23 (C = O). MS [+ESI]: m/z = 375 $[M+H]^+$, $C_{19}H_{22}N_2O_4S$ (Mw= 374.45 g/mol) = Calculated: C, 60.94%; H, 5.92%; N, 7.48%; S, 8.56% Found: C, 60.44%; H, 5.25%; N, 7.22%; S, 8.05%.

2-(6-hydroxyhexylthio)-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione (7c) was synthesized from 2-chloro-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione **(5)** (0.1 g, 2.033 mmol) and 6-Mercapto-1-hexanol **(6c)** (0.046 mL, 4.066 mmol) by use of the general procedure 1.

Purple viscous oil. Yield: 0.128 g (87%). R*f*: 0.56 [$CHCl_3$]. IR (KBr): 3385 (-OH), 3069 (-CH_{arom}), 2930, 2854, 2803 (C-H), 1667 (C = O), 1532 (C = C). ^{1}H-NMR (499.74 MHz, $CDCl_3$): δ = 1.10-1.51 (m, 8 H, -CH_2), 2.26 (s,3H, -NCH_3), 2.68 (t, J = 7.32, 4 H, -NCH_2), 2.83 (t, J = 6.84, 4 H, -NCH_2), 3.22 (m, 2 H, -OCH_2), 3.50 (t, J = 4.88, 2 H, -OCH_2), 7.74-7.93 (m, 4 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 25.44 (-CH_3), 28.12, 29.45, 32.87, 39.99 (-CH_2), 44.56 (-NCH_3), 51.79 (S-CH_2), 55.56, 60.68 (N-CH_2), 66.71 (-OCH_2), 154.58, 124.73, 126.01, 126.82, 132.36, 132.69, 133.59,134.28 (**C**$_{arom}$, **CH**$_{arom}$), 181.59, 181.57(C = O). MS [+ESI]: *m/z* = 389 $[M+H]^+$, $C_{21}H_{28}N_2O_3S$ (Mw= 388.52 g/mol) = Calculated: C, 64.92%; H, 7.26%; N, 7.21%; S, 8.25% Found: C, 64.54%; H, 7.13%; N, 6.95%; S, 9.14%.

2-(4-fluorophenylthio)-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione (7d) was synthesized from 2-chloro-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione **(5)** (0.1 g, 2.033 mmol) and 4-Fluorothiophenol **(6d)** (0.044 mL, 4.066 mmol) by use of the general procedure 1.

Purple viscous oil. Yield: 0.118 g (81%). R*f*: 0.49 [$CHCl_3$]. IR (KBr): 3062, 3014, 2938, 2799 (-CH), 1670 (C = O), 1591 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 2.24-2.49 (s, 3 H, -NCH_3), 2.51 (t, J = 7.32, 4 H, -NCH_2), 3.48 (t, J = 7.32, 4 H, -NCH_2), 6.99-7.93 (m, 8 H, H_{arom}).^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 44.93 (-NCH_3), 50.47, 54.47 (-NCH_2), 132.98, 131.94, 131.51, 130.30, 130.24, 130.12, 130.10, 129.10, 129.04, 125.75, 125.49, 115.20, 115.03 (C_{arom}, CH_{arom}),181.07, 180.63 (C = O). MS *[+ESI]: m/z* = 383 $[M+H]^+$, $C_{21}H_{19}FN_2O_2S$ (Mw= 382.45 g/mol) = Calculated: C, 65.95%; H, 5.01%; N, 7.32%; S, 8.38% Found: C, 65.54%; H, 5.20%; N, 7.21%; S, 8.58%.

2-(4-bromophenylthio)-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione (7e) was synthesized from 2-chloro-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione **(5)** (0.05 g, 2.033 mmol) and 4-Bromothiophenol **(6e)** (0.033 mL, 4.066 mmol) by use of the general procedure 1.

Purple viscous oil. Yield: 0.059 g (71%). R*f*: 0.50 [$CHCl_3$]. IR (KBr): 3073, 2937, 2843, 2797 (-CH), 1671 (C = O), 1530 (C = C).^{1}H NMR (499.74 MHz, $CDCl_3$): 2.24 (s, 3 H, -NCH_3), 2.50 (t, J = 7.32, 4 H, -NCH_2), 3.46 (t, J = 7.32, 4 H, -NCH_2), 7.20-7.97 (m, 8 H, H_{arom}).^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 44.85 (-NCH_3), 50.46, 54.41 (-NCH_2), 134.73, 134.58, 133.06, 131.98, 131.49, 131.21, 131.13, 131.05, 130.99, 128.42, 128.24, 125.88, 125.81, 118.85, 118.80 (C_{arom}, CH_{arom}),181.03, 180.38 (C = O). MS [+ESI]: *m/z* = 445 $[M+H]^+$, $C_{21}H_{19}BrN_2O_2S$ (M_w= 443.36 g/mol) = Calculated: C, 56.89%; H, 4.32%; N, 6.32%; S, 7.23% Found: C, 56.80%; H, 4.25%; N, 6.20%; S, 7.40%.

2-(4-methylpiperazin-1-yl)-3-(perfluorophenylthio)naphthalene-1,4-dione (7f) was synthesized from 2-chloro-3-(4-methylpiperazin-1-yl)naphthalene-1,4-dione **(5)** (0.05 g, 2.033 mmol) and pentafluorothiophenol **(6f)** (0.034 mL, 4.066 mmol) by use of the general procedure 1.

Purple Solid. Yield: 0.063 g (75%). Mp.: 124-125 °C. R*f*: 0.41 [$CHCl_3$]. IR (KBr): 3012, 2925, 2847 (C-H), 1674

(C = O), 1545 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 2.53 (s, 3 H, -NCH_3), 2.90 (s, 4 H, -NCH_2), 3.73 (t, J = 9.28, 4 H, -NCH_2), 7.84 (dd, J = 7.32, 8.29, 2 H, H_{arom}), 7.92 (dd, J = 6.35, 7.81, 2 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 44.28 (-NCH_3), 50.52, 54.18 (-NCH_2), 153.10, 149.25, 146.73, 144.12, 137.10, 135.75, 133.34, 131.30, 130.34, 132.47, 132.41, 131.30, 130.83, 131.20 (**C**$_{arom}$, **C**H$_{arom}$), 180.55, 179.18 (C = O). MS [+ESI]: *m/z* = 455 $[M+H]^+$, $C_{21}H_{15}F_5N_2O_2S$ (Mw = 454.41 g/mol) = Calculated: C, 55.51%; H, 3.33%; N,6.16%; S, 7.06% Found: C, 55.41%; H, 3.20%; N, 6.10%; S, 8.12%

2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione (9)[21] was synthesized from 2,3-Dichloro-1,4-Naphthoquinone (**1**) (1.0 g, 2.033 mmol) and 3-Amino-1,2-propanediol **(8)** (0.40 g, 2.033 mmol) by use of the general procedure 1.

Red Solid. Yield: 1.135 g (81%). Mp.: 137-138 °C. R*f*: 0.47 [EtAc]. IR (KBr): 3454 (-OH), 1644 (C = O), 1575 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 3.61 (m, 2 H,-NCH_2), 4.13(m, 2 H,-OCH_2), 6.36 (s, 1 H, >CH-OH),8.07-7.96 (d, J = 8.30, 2 H, H_{arom}), 7.67-7.54 (t, J = 7.32, 2 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 46.17 (-NCH_2), 63.31 (-OCH_2), 70.07 (>CHOH), 133.90, 131.54, 128.93, 125.86, 125.15 (C_{arom}, CH_{arom}), 179.50, 179.00 (C = O). MS [+ESI]: m/z = 280.0 $[M-H]^-$, $C_{13}H_{12}ClNO_4$ (M, 281.69) = Calculated: C, 55.43%; H, 4.29%; N, 4.97% Found: C 55.22%, H, 4.19%; N, 4.90%.

2-(2,3-dihydroxypropylamino)-3-(6-hydroxyhexylthio)-naphthalene-1,4-dione (11) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0.1 g, 0.355 mmol) and 6-Merkapto-1-Hexanol **(10)** (0.047 mL, 0.355 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.086 g (89%). R*f*: 0.65 [EtAc]. IR (KBr): 3373 (-NH, -OH), 2856, 2930 (-CH), 1675 (C = O), 1592 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 1.21-1.75 (m, 8 H, -CH_2), 3.55 (m, 4 H,-OCH_2), 2.60 (t, J = 7.32, 2 H,-SCH_2), 3.65 (m, 2 H,-NCH_2), 6.97 (s, 1 H, >CH-OH), 7.52-8.05 (m, 4 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 24.36, 27.18, 27.23, 31.52 (-CH_2), 46.94 (-NCH_2), 33.85 (-SCH_2), 61.73 (-OCH_2), 70.09 (>CHOH), 159.18, 133.60, 131.11, 125.52, (**C**$_{arom}$, **C**H$_{arom}$), 180.51, 179.04 (C = O). MS [+ESI]: *m/z* = 378.0 $[M-H]^-$, $C_{19}H_{25}NO_5S$ (M, 379.47) = Calculated: C, 60.14%; H, 6.64%; N, 3.69%, S, 8.45% Found: C 60,11%, H., 6.56%; N, 3.45%; S, 9.10%.

2-(2,3-dihydroxypropylamino)-3-(2-hydroxyphenylthio)-naphthalene-1,4-dione (13) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0.1 g, 0.355 mmol) and 2-Mercaptophenol **(12a)** (0.044 g, 0.355 mmol) by use of the general procedure 1.

Red Solid. Yield: 0.085 g (58%). Mp.: 153-154 °C. R*f*: 0.47 [EtAc]. IR (KBr): 3514 (-NH, -OH), 2853, 2920, 2948 (-CH), 1674 (C = O). ^{1}H NMR(499.74 MHz, $CDCl_3$): 3.60 (m, 4 H,-OCH_2), 3.77 (m, 2 H,-NCH_2), 6.92 (s, 1 H, >CH-OH), 7.56-8.09 (m, 8 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 45.86 (-NCH_2), 63.32 (-OCH_2), 70.07 (>CHOH), 133.91, 133.90, 131.54, 131.50, 125.85 (**C**$_{arom}$, **C**H$_{arom}$), 179.50, 179.05 (C = O). MS [+ESI]: *m/z* = 372 $[M+H]^+$, $C_{19}H_{17}NO_5S$ (Mw= 371.41 g/mol) = Calculated: C, 61.44%; H, 4.61%; N, 3.77%, S, 8.63% . Found: C 61.04%, H, 4.83%; N, 3.33%; S, 8.05%

2-(2,3-dihydroxypropylamino)-3-(3-hydroxybutan-2-ylthio) naphthalene-1,4-dione (15) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0,1 g, 0.355 mmol) and 3-Mercapto-2-butanol **(14)** (0.037 g, 0.355 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.098 g (71%). R*f*: 0.43 [EtAc] IR (KBr): 3381 (sb, -NH, -OH), 2871, 2929, 2972 (-CH), 1719, 1655 (C = O), 1555 (C = C). ^{1}H NMR (499.74 MHz, $CDCl_3$): 1.21-1.18 (d, 6 H, -CH_3), 3.77 (m, 4 H,-OCH_2), 2.74 (m, 2 H,-SCH_2), 4.08 (m, 2 H,-NCH_2), 5.26 (s, 1 H, >CH-OH), 7.20-7.64 (m, 4 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 12.66, 15.88 (-CH_3), 52.19 (NCH_2), 37.71(-SCH), 66.99 (-OCH_2), 69.32 (>CHOH), 75.76 (-OCH), 131.42, 129.87, 127.78 (**C**$_{arom}$, **C**H$_{arom}$),180.20, 179.80 (**C**=O). MS [+ESI]: *m/z* = 352$[M+H]^+$, $C_{17}H_{21}NO_5S$ (Mw= 351.42 g/mol) = Calculated: C, 58.10%; H, 6.02%;N, 3.99%, S, 9.12% Found: C 58.02%, H, 6.44%; N, 3.55%; S, 10.01%.

2-(2,3-dihydroxypropylamino)-3-(2-hydroxypropylthio)-naphthalene-1,4-dione (17) was synthesized from 2-(2,3-dihydroxypropylamino()-3-chloronaphthalene-1,4-dione **9)**[21] (0.1 g, 0.355 mmol) and 1-Mercapto-2-propanol **(16)** (0.033 g, 0.355 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.082 g (61%). R*f*: 0.48 [EtAc]. IR (KBr): 3346 (-NH, -OH), 2929 (-CH), 1679 (C = O), 1550 (C = C).^{1}H NMR (499.74 MHz, $CDCl_3$): 1.20-1.51 (m, 3 H, -CH_3), 2.52-2.55 (m, 2 H,-SCH_2), 4.09-4.25 (m, 2 H,-OCH_2), 3.54-3.57 (m, 2 H, -NCH_2), 4.79 (s, 1 H, >CH-OH), 7.62-7.66 (dd, J = 8.78, 8.78, 2 H, H_{arom}), 7.67-7.54 (t, J = 7.32, 2 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 46.68 (-NCH_2), 63.34 (-OCH_2), 67.17 (>CHOH), 166.73, 133.88, 131.47, 129.82, 127.79, 108.75 (C_{arom}, CH_{arom}), 180.51, 179.04 (C = O). MS [+ESI]: m/z = 371 $[M+Cl]^-$, $C_{16}H_{19}NO_5S$ (Mw= 337.39 g/mol) Calculated: C, 56.96%; H, 5.68%; N, 4.15%, S, 9.50% Found: C 56.90%, H, 5.60%; N, 4.22%; S, 10.02%.

2-(2,3-dihydroxypropylamino)-3-(4-fluorophenylthio)-naphthalene-1,4-dione (19a) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0,065 g, 0.231 mmol) and 4-Fluorothiophenol **(18a)** (0.029 g, 0.231 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.63 g (86%). R*f*: 0.37 [EtAc]. IR (KBr): 3274 (-NH, -OH), 3019, 2937 (-CH), 1687 (C = O), 1549 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 3.61- 3.66 (m, 2 H,-NCH_2), 4.09-4.13(m, 2 H,-OCH_2), 7.23-8.09 (m, 8 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 46.37 (-NCH_2), 63.28 (-OCH_2), 69.72 (>CHOH), 134.08, 131.40, 126.13, 125.74, 115.33, 115.15 (C_{arom}, CH_{arom}), 180.07, 179.80 (C = O). MS [+ESI]: *m/z* = 374 $[M+H]^+$, $C_{19}H_{16}FNO_4S$ (M_w= 373.40 g/mol) Calculated: C, 61.12%; H, 4.32%; N, 3.75%; S, 8.59%; Found: C 61.20%, H, 4.30%; N, 3.58%; S, 9.05%.

2-(2,3-dihydroxypropylamino)-3-(4-bromophenylthio)-naphthalene-1,4-dione (19 b) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0.065 g, 0.231 mmol) and 4-Bromothiophenol **(18 b)** (0.383 g, 0.231 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.069 g (%78). R*f*: 0.39 [$CHCl_3$]. IR (KBr): ν = 3346 (-NH, -OH), 3019, - 2929 (C-H), 1679 (C = O), 1587 (C = C). ^{1}H NMR (499.74 MHz, $CDCl_3$): 3.49-3.61 (m, 2 H,-NCH_2), 4.19-4.15(m, 2 H,-OCH_2), 4.79 (s, 1 H, >CH-OH), 7.28 (dd, J = 6.34, 6.83, 2 H, H_{arom}), 7.36 (dd, J = 6.34, 6.83, 2 H, H_{arom}), 7.36-8.08 (m, 4 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 44.93 (-NCH_2), 63.53 (-OCH_2), 67.31 (>CHOH), 134.90, 134.75, 131.61, 131.39, 131.29, 131.26, 128.93, 128.54 (C_{arom}, CH_{arom}), 180.44, 166.87 (C = O). MS [+ESI]: *m/z* = 433 $[M]^+$, $C_{19}H_{16}BrNO_4S$ (M_w=434.30 g/mol) = Calculated: C, 52.54%; H, 3.71%, N, 3.23%; S, 7.38. Found: C, 52.44%; H, 3.55%, N, 3.40%, S, 8.07.

2-(2,3-dihydroxypropylamino)-3-((2-(hydroxymethyl)-phenyl)sulfanyl) naphthalene-1,4-dione (20) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0.1 g, 0.355 mmol) and 2-Mercaptobenzyl alcohol **(12 b)** (0.05 g, 0.355 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.102 g (68%). R*f*: 0.42 [$CHCl_3$]. IR (KBr): ν = 3326 (-NH, -OH), 3062, 3014, 1938, 2846 (-CH), 1670 (C = O), 1592 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 3.39- 3.44 (m, 4 H,-OCH_2), 2.49-2.51 (m, 4 H,-NCH_2), 6.81-8.01 (m, 8 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 44.93 (-NCH_2), 50.47 (-OCH_2), 54.47 (>CHOH), 159.60, 152.81, 132.98, 131.94, 131.51, 130.12, 129.10, 125.49 (C_{arom}, CH_{arom}), 181.77, 180.63 (C = O). MS [+ESI]: *m/z* = 383[M-H]$^-$, $C_{20}H_{19}NO_5S$ (M_w= 385.43 g/mol) = Calculated: C, 62.32%; H, 4.97%,N, 3.63%; S, 8.32. Found: C, 62.20%; H, 4.65%, N, 3.80%, S, 8.45.

Butyl 3-(2-(2,3-dihydroxypropylamino)-1,4-dihydro-1,4-dioxonaphthalen-3-ylthio)propanoate (21) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0.1 g, 0.355 mmol) and Butyl-3-mercapto-propionate **(6a)** (0.06 mL, 0.355 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.061 g (77%). R*f*: 0.28 [$CHCl_3$]. IR (KBr): 3416 (-NH, -OH), 2959, 2931 (-CH), 1731 (C = O_{ester}), 1675 (C = $O_{quinone}$), 1556 (C = C). ^{1}H NMR(499.74 MHz, $CDCl_3$): 0.82-0.86 (m, 3 H, -CH_3), 1.18-1.51 (m, 4 H, -CH_2), 3.94-4.13 (m, 4 H,-OCH_2), 3.61 (m, 2 H,-NCH_2), 6.94 (s, 1 H, >CH-OH), 3.58 (m, 2 H,-SCH_2), 7.44-8.09 (m, 4 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 18.12, 28.80, 29.51, 29.60, 29.63 (-CH_2, -CH_3), 47.24 (-NCH_2), 33.19 (-SCH_2), 63.45, 63.57 (-OCH_2), 70.06 (>CHOH), 159.82, 133.64, 132.54, 131.20, 129.85, 125.55 (C_{arom}, CH_{arom}), 180.44, 178.86, 171.48 (C = O). MS [+ESI]: *m/z* = 406 [M-H]$^-$,$C_{20}H_{25}NO_6S$ (M_w= 407.48 g/mol) Calculated: C, 58.95%; H, 6.18%, N, 3.44%; S, 7.87. Found: C, 58.88%; H, 6.08%, N, 3.34%, S, 8.40.

(23) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0.1 g, 0.355 mmol) and 2,2'-(ethylendiokxy)-bis(ethylenediamine) **(22)** (0.052 mL, 0.355 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.079 g (51%). R*f*: 0.37 [$CHCl_3$]. IR (KBr): ν = 3431 (-NH), 3018, 2926, 2854 (-CH), 1675 (C = O), 1573 (C = C). ^{1}H NMR (499.74 MHz, $CDCl_3$): 2.23-2.29 (m, 4 H,-NCH_2), 3.54-4.24 (m, 8 H,-OCH_2), 7.19-8.10 (m, 4 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 45.89, 46.55 (-NCH_2), 63.34, 67.99 (-OCH_2), 150.83, 133.87, 132.64, 131.57, 130.51, 128.91 (C_{arom}, CH_{arom}),179.50, 179.00 (C = O). MS [+ESI]: *m/z* = 325 $[M + Na]^+$, $C_{16}H_{18}N_2O_4$ (M_w= 302.33 g/mol) = Calculated: C, 63.56%; H, 6.00%, N, 9.27%. Found: C, 63.51%; H, 5.93%, N, 9.21%.

2-(2-methylundecan-2-ylthio)-3-ethoxynaphthalene-1,4-dione (25) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0,065 g, 2.033 mmol) and tetradodedcylmercaptan **(24)** (0.072 mL, 2.033 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.112 g (65%). R*f*: 0.48 [EtAc]. IR (KBr): 3068, 2959, 2872 (C-H), 1674 (C = O), 1593 (C = C). ^{1}H NMR (499.74 MHz, $CDCl_3$): 0.67-0.82 (m, 12 H, -CH_3), 1.18-1.82 (m, 16 H, CH_2), 4.55 (m, 2H, -OCH_2),7.63 (t, J = 5.37, 2H, H_{arom}), 8.03 (d, 2 H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 13.38, 13.58, 30.91, 31.57 (-CH_3), 45.68, 38.45, 37.49, 9.17, 28.68 (-CH_2), 64.65 (-OCH_2), 132.43, 132.14, 132.00, 131.38, 131.14, 129.91 (**C**$_{arom}$, **C**H_{arom}), 180.01, 179.80 (C = O). MS [+ESI]: *m/z* = 425 $[M + Na]^+$, $C_{24}H_{34}O_3S$ (M_w= 402.59 g/mol); Calculated: C, 71.60%; H,8.51%; S, 7.96% Found: C 71.50%, H, 8.45%; S, 8.16% .

Methyl 3-(2-(2,3-dihydroxypropylamino)-1,4-dihydro-1,4-dioxonaphthalen-3-ylthio)propanoate (26) was synthesized from 2-(2,3-dihydroxypropylamino)-3-chloronaphthalene-1,4-dione **(9)**[21] (0.065 g, 0.231 mmol) and Methyl-3-mercaptopropionate **(6 b)** (0.027 mL, 0.231 mmol) by use of the general procedure 1.

Red viscous oil. Yield: 0.068 g (88%). R*f*: 0.42 [$CHCl_3$]. IR (KBr): ν = 3320 (-NH, -OH), 2926, 2958 (-CH), 1729 (C = O_{ester}), 1630 (C = $O_{quinone}$), 1592 (C = C). ^{1}H NMR (499.74 MHz, $CDCl_3$): 2.20-2.83 (m, S- CH_2), 3.44-3.86(m,-N- CH_2), 4.25-4.60 (m, HO-CH-), δ = 4.96-5.20 (m, HO-CH_2-), 7.24-7.96 (d, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): 39.49 (S- CH_2-), 40.25 (S-CH-), 47.49 (N- CH_2-), 51.83 (-CH_3-O), 66.25 (-CH_2-OH), 70.24 (-CH-OH), 126.63, 132.76, 135.10 (**C**$_{arom}$, **C**H_{arom}), 180.44, 179.88, 172.39 (C = O). MS [+ESI]: *m/z* = 387 $[M + Na]^+$, $C_{17}H_{19}O_6NS$ (M_w= 365.4 g/mol) = Calculated: C, 55.88%; H, 5.24%, N, 3.83%; S, 8.78.Found: C, 55.64%; H, 5.22%, N, 3.68%, S, 9.10.

Conclusions

In present study the reactions of some quinones with amino alcohols and thiols were investigated. The structures of all compounds were characterized by spectroscopic methods (FT-IR, ^{1}H NMR, ^{13}C NMR, Mass) and microanalysis. The absorption behaviors of novel compounds were investigated with UV-Vis spectroscopy in different solutions such as ethanol, tetrahydrofuran and chloroform.

Disclosure statement

No potential conflict of interest was reported by the authors.

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